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(21) International Application Number: PCT/US00/10665 (22) International Filing Date: 20 April 2000 (20.04.00) (30) Priority Data: 09/294,143 20 April 1999 (20.04.99) US (71)(72) Applicants and Inventors: BATARSEH, Kareem [JO/US]; 82 J Airport Boulevard, Morgantown, WV 26505 (US). AL-KAYED, Marwan [JO/JO]; P.O. Box 413, Naour, Amman (JO). (74) Agent: KILYK, Luke, A.; Kilyk & Bowersox, P.L.L.C., 3603 E Chain Bridge Road, Fairfax, VA 22030 (US).		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: MICROBICIDAL FORMULATIONS AND METHODS FOR CONTROLLING MICROORGANISMS (57) Abstract <p>Microbicidal formulations are described which are preferably ecologically friendly and non-toxic to mammals, and are highly effective against a broad spectrum of detrimental pathogenic microorganisms. The microbicidal formulation contains complexes having the formula R-M, wherein R is at least one organic chelating moiety and M is at least one metal ion which is microbicidal to at least one microorganism. These complexes can disrupt microorganism activities by penetrating the natural protecting bio-films of such microorganisms through the reaction of the R-group with the organic constituents of these microorganisms while releasing M into their intra-cellular media. Thus, this process exhibits its biocidal activities from the inside-out, contrary to other methods which rely on damaging the protective biofilms. These microbicidal formulations can be diluted in suitable proportions into aqueous systems to produce the desired dosages for each individual case, depending on the level and the severity of the contamination. The microbicidal formulations can be applied by conventional methods, e.g., spraying, soaking, fogging, impregnation, and the like.</p>		

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MICROBICIDAL FORMULATIONS AND METHODS FOR CONTROLLING MICROORGANISMS

The present invention relates in general to controlling microbicides and more particularly relates to microbicides which are preferably environmentally friendly and non-toxic to mammals and which are highly effective against viruses, amoebae, bacteria (both gram-negative and -positive), fungi, algae, spores, and the like.

BACKGROUND OF THE INVENTION

Water is the most important element of life since it comprises almost 80% of the human body. In addition, food hygiene depends solely on water, and therefore contamination of water is a common vehicle for the transport of epidemic diseases to humans like Typhoid, food poisoning, and Dysentery. For example, Psychrophilic bacteria whose presence in the microflora in water can affect refrigerated food and spoil it. Hence, water contamination cannot be overlooked and extreme measures should be taken to assure a high quality of water to sustain life.

With the advent of technology, clean water is becoming a scarce commodity. Water contamination is unequivocally becoming a worldwide problem with unknown ramifications, and billions of US dollars are spent annually to improve its quality. Contamination of waters is not only restricted to industrialized countries, but also to developing nations as well. Therefore, there is an immediate need to find poignant solutions to maintain and preserve water sources.

Recently, there has been a growing interest among scientists and engineers to develop new water and food disinfectant technologies to clean water from dangerous microorganisms. Various methods have been employed which are divided into two categories; namely, physical, chemical, or both. The physical category is represented by techniques utilizing ultrafiltration, reverse osmosis, radiation, freezing, heating, and ultrasound. Although these methods have proved to be effective, the drawbacks include the large electricity requirements and expensive equipment. On the other hand, the chemical category relies on the use of chemical adjuvants which exhibit biocidal properties such as aldehydes, phenols, alcohol, potassium permanganate, and chlorine and certain chlorine containing compounds. Some of these chemicals have many disadvantages associated with them and are now considered poisonous compounds. For instance, people coming into contact with these substances can develop skin irritation and suffer from long time illnesses which in some cases can be fatal; not to mention the unpleasant taste and odor associated with these chemicals. In addition, formation of mutagenic and carcinogenic agents, and genetic resistance are also some of their disadvantages.

Notwithstanding, such compounds have afforded a way to battle these harmful microorganisms and their effectiveness have been unequivocally demonstrated.

Other methods have relied upon the use of ultra-violet irradiated silver fluoride solutions containing colloidal silver as a source of germicide activities, such as U.S. Patent No. 3,422,183, incorporated herein in its entirety by reference. However, such techniques require expensive equipment and large amounts of electricity.

Hydrogen peroxide is a highly oxidizing agent, and it has been used the past 40 years as a disinfectant. Its main advantage is that it does not produce toxic residue or by-products. It has been used ubiquitously as an indirect food additive, as a disinfectant in hospitals, as a

decontamination and purification agent of industrial waste water, and as a cleaning agent for exhaust air. Nonetheless, it decomposes readily to form water and oxygen, and has high sensitivity to sunlight and UV rays. Therefore, it is not suited for long-term use since recontamination cannot be circumvented.

5 In 1880, the Swiss botanist Carl van Nageli observed that highly diluted silver solutions have an algicidal effects. To describe this effect he coined the term "Oligodynamic". Colloidal silver, which is a pure, all-natural substance consisting of sub-microscopic clusters of silver ions held in suspension in de-ionized water by tiny positive charges on the silver ions, is a powerful prophylactic antibiotic which was used for years with no known side effects. It acts
10 as an inhibitor disabling particular enzymes which bacteria, fungi, and viruses used in their mode of metabolism.

Based on this oligodynamic property, U.S. Patent No. 4,915,955, incorporated in its entirety herein by reference, combines the germicidal effects of hydrogen peroxide with colloidal silver, an inorganic acid and an organic stabilizer at concentrations of 10-35 mg/l
15 against many forms of bacteria and viruses. The process is based on silver ions, with the aid of hydrogen peroxide, damaging the protective biofilms of these microorganisms. Hence, this method depends solely on killing germs intercellularly.

SUMMARY OF THE INVENTION

20 The present invention relies on using metal ions (M). A chemical matrix or complex is formed wherein these metal ions are attached to an organic-chelating moiety (R), to be used in stoichiometric amounts or more to form complexes, which serves as carriers for M into the intra-cellular medium of such microorganisms. These concentrated complexes can then be

mixed with water to form suitable disinfectants. This process is different from previous methods found in the literature where the metal ion remains freely suspended in solution.

It is to be understood that the preceding general discussion and the discussion which follows are considered explanatory and exemplary in nature, and are solely intended to give
5 additional merits of the current invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention provides a suitable concentrate of organo-metal compounds that form suitable disinfectants upon admixing with water or other aqueous sources. The basic
10 principle that governs the formation of such a concentrate is the fact that the metal ions are attached to an organic-chelating R group used in stoichiometric amounts or more that forms organic complexes. These organic complexes can penetrate the protective biofilms of germs and other microorganisms. Once the R-M complex is inside the biofilm, it can then exhibit its germicidal or biocidal effects by releasing M into their intra-cellular media and, hence, disrupt
15 microbial activities. In the most general terms, this scenario can be depicted as giving these germs a "poisonous pill." Thus, unlike other methods which attribute their biocidal effects through damaging the protective biofilms (from the outside-in, i.e., inter-cellularly), the present invention does the opposite; specifically, killing microorganisms from the inside-out, i.e., intra-cellularly.

20 To enhance its activity, the concentrated organic complex can be mixed with other disinfectants, including, but not limited to, isopropanol, chlorhexidine gluconate, chlorhexidine digluconate, chlorhexidine dihydrochloride, chlorhexidine diacetate, and/or hydrogen peroxide, though it is not necessary. In addition, natural and artificial color and flavor additives can be

added as well.

Of course, the microbicidal formulations of the present invention can be used either directly, by introduction to a system, e.g., a swimming pool, or can be diluted with aqueous solutions, like distilled and/or deionized water to provide the necessary biocidal activity, depending on the application.

With respect to the organic complex, R-M, the R group is an organic group which can complex with one or more metal ions, and is preferably a group which is amphoteric. Also, the R group is preferably of a chemical nature which microorganisms would find nourishable. Preferably, the R group can be at least one amino acid or can be formed from at least one amino acid. The amino acids are preferably amphoteric, that is, they can react either as acids or as bases, depending on the circumstances. They exist primarily as neutral dipolar ions or zwitterions ($Z = H_3N^+-CRH-COO^-$). Hence, at low pH, the zwitterions exist as cations, and at high pH they exist as anions; therefore at a certain pH, the amino acids preferably exist primarily as zwitterions. This point is called the isoelectric point which depends on the structure of the given amino acid. Primary, secondary, or tertiary amines can all be used here as long as the amine is compatible with (M) in the formation of the complex. The amino acids are preferably chosen so as to make use of the lone pair of electrons on the nitrogen atom where the metal ions (the Lewis acid, electron pair acceptor) can form dative covalent bonds (also known as a coordinate covalent bond) with the carboxylic group of the amino acid. In essence, these metal ions, or Lewis acids, can share an electron pair donated by the amino acid, that is, the ligand, or Lewis base. Preferably, the double bonded oxygen of the carboxylic group of the amino acid is complexed (or forms a dative covalent bond with the double bonded oxygen) to the metal (M), and not to the hydroxy group of the carboxylic group of the amino acid. This

is preferably accomplished by forming the complex under low pH conditions (e.g., acidic conditions) and preferably at pH conditions of pH 2.0 or less and more preferably at a pH 1.0 or less.

Preferably, examples of amino acid compounds which can be used to form the R group include, but are not limited to, α -amino acids. Specific examples include, but are not limited to, isoleucine, phenylalanine, leucine, lysine, methionine, threonine, tryptophan, valine, alanine, glycine, arginine, histidine, hydroxyproline, γ -aminobutyric acid, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, phenylalanine, proline, serine, tyrosine, and derivatives thereof and mixtures thereof.

With respect to the other part of the complex which is M, M represents at least one metal ion which is microbicidal to at least one microorganism. Preferably, the metal ion is microbicidal to a multitude of microorganisms. Examples of the metal ion include, but are not limited to, silver, copper, zinc, mercury, manganese, chromium, nickel, cadmium, arsenic, cobalt, aluminum, lead, selenium, platinum, gold, titanium, tin, and the like. More than one type of R group and more than one type of M can be used to form the R-M complex, also, mixtures of different R-M complexes can also be used.

The complex of the present invention can be prepared by forming the metal ion from a metal salt compound and the organic chelating moiety from an organic compound which is preferably an amine, and more preferably an amino acid. In the preferred process of making the organic complex of the present invention, a metal salt compound is mixed with at least one inorganic acid preferably at room temperature and preferably in the presence of an aqueous solution like a distilled and deionized water. Then, at least an equimolar basis of the organic containing compound such as an amino acid is added to form the metal complex preferably

while homogenizing the mixture. This preparation preferably occurs under low pH conditions, such as pH of about 2.0 or less and more preferably at a pH of 1.0 or less. The resulting solution can then be further diluted with aqueous solution and preferably distilled and deionized water and further disinfectants or other additives can be added to form the microbicidal composition of the present invention. The pH of the resulting solution can then be raised, such as by adding water.

According to the present invention, controlling the growth of at least one microorganism includes both the reduction and/or prevention of such growth. It is to be further understood that by "controlling," the growth of at least one microorganism is inhibited. In other words, there is no growth or substantially no growth of at least one microorganism.

"Controlling" the growth of at least one microorganism includes maintaining a microorganism population at a desired level (including undetectable levels such as zero population), reducing a microorganism population to a desired level, and/or inhibiting or slowing the growth of at least one microorganism. Thus, materials and mediums susceptible to attack by at least one microorganism are preserved and/or protected from this attack and the resultant deleterious effects. The present invention also provides a method for controlling the growth of at least one microorganism in or on a material or medium susceptible to attack by the microorganism which comprises the step of adding to the material or medium a composition of the present invention in an amount effective to control the growth of the microorganism.

The mode as well as the rates of application of the composition of this invention could vary depending upon the intended use. The composition could be applied by spraying or brushing onto the material or product. The material or product in question could also be treated by dipping in a suitable formulation of the composition. In a liquid or liquid-like medium, the

composition could be added into the medium by pouring or by metering with a suitable device so that a solution or dispersion of the composition can be produced. Thus, the substrates or materials susceptible to attack by these types of microorganisms are preserved from this attack and the resulting spray or other detrimental effects caused by the microorganisms. Further, it is to be understood that "controlling" the growth of at least one microorganism also includes biostatically reducing and/or maintaining a low level of microorganisms such that the attack by microorganisms and any resulting spoilage or other detrimental effects are eliminated, i.e., the microorganism growth rate or microorganism attack rate is slowed down or eliminated.

Microorganisms, as used herein, include, but are not limited to bacteria, fungi, algae, viruses, amoebae, spores, and the like, and include both yeasts and molds.

Preferably, at least an equimolar portion of the chosen amino acid is used in preparing the solution, preferably in excess of the sequester univalent metal ions (e.g., Ag); at least twice as much for bivalent metals (e.g. Cu), and so on. Any source of ionic M in the form of salts can be used in the present invention. For the case of silver, colloidal silver can be used as well.

The present invention is further illustrated by the following examples. These experiments constitute some of the embodiments of the invention herein disclosed. After the preparation of these disinfectants according to the present technique, their efficacy with respect to toxicity was then tested and evaluated against a broad spectrum of pathogenic microorganisms.

METHODOLOGY

I. Chemical

Under minimum light, and at room temperature, a silver ion solution of 1.1×10^5 ppm was prepared by dissolving 400 mg of silver nitrate in 2.045 ml of double distilled-de-ionized water and 0.255 ml of 85% phosphoric acid. This solution was then used for the proceeding experiments.

Example I

By using a micropipet, 230 μ l of the above prepared solution was placed in a microtube where 34.61 mg of glutamic acid was added, and the mixture was stirred thoroughly. This amount of glutamic acid represents an equimolar amount of amino acid with respect to the silver ions in the above prepared solution. Instantly, an insoluble material was observed. This insoluble dispersant has microbial killing activities. This prepared solution was then mixed with 50 ml of double distilled-de-ionized water. The solution was mixed continuously until homogenization was achieved. Then, the product was poured into a dark bottle. This desired product can be added to or proportioned into aqueous systems and diluted to achieve the required germicidal potency, depending on its intended use.

Example II

The same procedure above was duplicated, but the amino acid used was leucine instead of glutamic acid. The amount of leucine used in this case was 30.84 mg which again represents an equimolar amount of the acid with respect to the silver ions.

Example III

The same procedure from Example I was again repeated, but the amino acid used was arginine. The amount of arginine used in this case was 40.97 mg which again represents an equimolar amount.

- 5 To study the effect of hydrogen peroxide on increasing the potency of these disinfectants, the three prepared solutions (Example I-III) were mixed with 50 ml of 50% H_2O_2 rather than water. Again, these prepared solutions were poured into dark bottles.

II. Biological

- 10 The above steps conclude the preparation of these disinfectants. However, to utilize these mixtures as bactericides, 5 ml of each bottled solution was added to 45 ml of double distilled-de-ionized water (10% by volume). Without the presence of H_2O_2 , this constitutes an active concentration of about 51 ppm of complex silver which proved to be sufficient to readily kill bacteria. The upper and lower concentration limits may be different if desired, depending
15 on the nature of the desired application. For the samples where H_2O_2 is present, the active concentration of the disinfectant should be around 56,000 ppm.

- The diluted solutions were then tested on several kinds of actively growing pathogenic bacteria to ascertain their effectiveness. Different strains of pathogenic bacteria were employed for the testing; namely, *E.coli*, *Stafelococus*, *Bascillus*, and *Salmonella*. For all the bacteria
20 used, the microbial killing activity was readily observed. The arginine-complex showed the most potency followed by the leucine-complex, and finally the glutamic acid-complex.

With respect to the presence of H_2O_2 in relation to its absence, the difference on the average was roughly around 3 times greater even though the active concentration was almost 1058 times greater than that for the case of an absence of H_2O_2 . The difference in biocidal

activity is not reflected in this value (1098 times greater while the increase is tripled). This is indicative that the biocidal activity is almost solely due to the R-M complex of the present invention. The order of efficacy with respect to the amino acid used was the same as when H_2O_2 was absent.

5 The biocides described herein have a plethora of applications and uses. They are suitable for the sterilization of drinking water, suitable for the beverage and food industry, suitable for sterilizing exposed surfaces, exhaust air and ventilation components, animal feed, suitable for use in the pharmaceutical industry, in hospitals, for surgical equipment, in swimming pools, in saunas, and for fish, poultry, and cattle farming, and the like.

10 The previous explanation and the illustrations and procedures set forth above are solely intended for the purpose of setting out the generic and general embodiments of the present invention. Therefore, it is to be understood that the invention by no means is limited to the specific features disclosed herein, and such details can be varied by those skilled in the art in consideration of the present specification and practiced without departing from the true scope
15 and merits of the invention.

Having thus described the present invention, the true scope and spirit of it is therefore presented by the following claims:

WHAT IS CLAIMED IS:

1. A microbicidal composition comprising a complex of the formula R-M, wherein R is at least one organic chelating moiety and M is at least one metal ion, and where R is present in an at least equimolar amount based on the amount of M, and M is microbicidal to at least one microorganism.
2. The microbicidal composition of claim 1, further comprising an aqueous solution.
3. The microbicidal composition of claim 1, wherein said at least one metal ion is a silver ion.
4. The microbicidal composition of claim 1, wherein said at least one metal ion of copper, zinc, mercury, chromium, manganese, nickel, cadmium, arsenic, cobalt, aluminum, lead, selenium, platinum, gold, titanium, tin, and combinations thereof.
5. The microbicidal composition of claim 1, wherein said at least one organic chelating moiety comprises at least one amino acid.
6. The microbicidal composition of claim 1, further comprising at least one disinfectant.
7. The microbicidal composition of claim 1, wherein said at least one organic chelating moiety is formed from an alpha-amino acid.
8. The microbicidal composition of claim 1, wherein said at least one organic chelating moiety is selected from isoleucine, phenylalanine, leucine, lysine, methionine, threonine, tryptophan, valine, alanine, glycine, arginine, histidine, and mixtures thereof.

9. A method to control the growth of microorganisms comprising contacting the microorganisms with a microbicidal composition comprising the microbicidal composition of claim 1, and wherein said composition kills said microorganisms intracellularly.

10. A method to control biofouling in a system, comprising introducing an effective amount of said microbicidal composition of claim 1 to said system to control said biofouling.

11. The microbicidal composition of claim 1, wherein the molar ratio of R to M is from about 1:1 to about 2:1.

12. The microbicidal composition of claim 2, wherein said microbicidal composition is present in said aqueous solution at a concentration of from about .001% to about 10% by total volume.

13. A method to prepare the microbicidal composition of claim 1 comprising dissolving a salt containing metal in at least one inorganic acid and an aqueous source; and adding at least one organic chelating compound containing R to form a metal complex having the formula R-M, wherein the preparation of the composition occurs at a pH of about 2.0 or less.

14. The microbicidal composition of claim 6, wherein said at least one disinfectant comprises one or more of chlorhexidine gluconate, chlorhexidine digluconate, chlorhexidine dihydrochloride, and chlorhexidine diacetate.

15. The microbicidal composition of claim 6, wherein said at least one disinfectant comprises one or more of isopropyl alcohol and hydrogen peroxide.

16. A microbicidal composition comprising a product obtained by combining at least one metal ion (M) with at least an equimolar amount of at least one organic chelating moiety (R) based on the amount of M, wherein M is microbicidal to at least one microorganism.

17. The microbicidal composition of claim 16, wherein said at least one organic chelating moiety comprises an amino acid.
18. The microbicidal composition of claim 16, wherein said at least one metal ion
5 is a silver ion.
19. A method to control the growth of a microorganism susceptible to treatment with a metal ion, said method comprising:
treating said microorganism with the microbicidal composition of claim 16.
20. A method of controlling biofouling in a system, comprising introducing to said
10 system an effective amount of the microbicidal composition of claim 16.
21. A microbicidal composition comprising a complex of the formula R-M, wherein R is at least one organic chelating moiety and M is at least one metal ion, and where R is present in an at least equimolar amount based on the amount of M, and M is microbicidal to at least one microorganism, wherein said at least one organic chelating moiety is formed from an
15 amino acid, and said organic chelating moiety has a carboxylic group which forms a dative covalent bond with M.
22. The microbicidal composition of claim 21, wherein M is complexed through the doubled bonded oxygen of the carboxylic group.

INTERNATIONAL SEARCH REPORT

b. National Application No
PCT/US 00/10665

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A01N59/16 A01N47/44 A01N37/44		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, PAJ, CHEM ABS Data, EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 01231 A (UNILEVER NV ;UNILEVER PLC (GB); CARR STUART WILLIAM (GB); LAMBERT) 18 January 1996 (1996-01-18) page 5, last paragraph -page 6, paragraph 1; claims 1,7; example 1 page 3, paragraph 2 - paragraph 3 page 1 -page 2, paragraph 2	1-3, 9-12,16, 18-20
X	DE 16 42 001 A (DEUTSCHE KATADYN GMBH) 22 April 1971 (1971-04-22) the whole document	1-3,6, 9-12,16, 18-20
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Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">19 September 2000</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">02/10/2000</div>
Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold; margin-top: 10px;">Muellners, W</div>

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 396 413 A (MILLER GEORGE A ET AL) 2 August 1983 (1983-08-02)</p> <p>column 1, line 10 - line 49; tables I,,III column 15, line 13 - line 33 column 16, line 23 - line 26 column 17, line 39 - line 44; claims</p>	<p>1-4,6, 9-12,15, 16,18-20</p>
X	<p>FR 2 728 143 A (SODIFRA) 21 June 1996 (1996-06-21)</p> <p>page 4, line 9 -page 6, line 5; claims</p>	<p>1-3,6, 9-12,15, 16,18-20</p>
X	<p>WO 94 04167 A (US GOVERNMENT) 3 March 1994 (1994-03-03)</p> <p>page 6, last paragraph -page 7, paragraph 2; table III page 9, line 22 -page 10, line 12; claims</p>	<p>1,2,4,6, 9-12,15, 16,19,20</p>
X	<p>WO 97 02038 A (CAPELLI CHRISTOPHER C) 23 January 1997 (1997-01-23)</p> <p>page 5, line 11 - line 24 page 10 -page 13, line 24 page 18, line 25 -page 19, line 8; claims 1,8,9; examples 6,13</p>	<p>1-3,6, 9-12,14, 16,18-20</p>
X	<p>PATENT ABSTRACTS OF JAPAN vol. 1995, no. 08, 29 September 1995 (1995-09-29) & JP 07 138167 A (SANGI CO LTD), 30 May 1995 (1995-05-30) abstract</p>	<p>1-5, 7-12, 16-22</p>
X	<p>PATENT ABSTRACTS OF JAPAN vol. 1999, no. 03, 31 March 1999 (1999-03-31) & JP 10 338605 A (NIKKO:KK;SUMITOMO CHEM CO LTD), 22 December 1998 (1998-12-22) abstract</p>	<p>1-3,5-7, 9-12, 15-22</p>
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A	<p>column 1 -column 2, line 7; claims; examples</p>	
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